

***Ab initio* pressure-dependent vibrational and dielectric properties of chalcopyrite CuAlS<sub>2</sub>**

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We have performed an *ab initio* study of pressure-dependent lattice dynamical properties of chalcopyrite semiconductor CuAlS<sub>2</sub>. The calculations have been carried out within the local density functional approximation using norm-conserving pseudopotentials and a plane-wave basis. Born effective charge tensors, dielectric permittivity tensors, the phonon frequencies at the Brillouin zone center, and their Grüneisen parameters are calculated using density functional perturbation theory. We compare the Grüneisen parameters of the calculated quantities with those of zinc-blende type materials and found similar trends.

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**I. INTRODUCTION**

The ternary I-III-VI<sub>2</sub> chalcopyrites form a large group of semiconductors with diverse structural, electrical, and optical properties.<sup>1,2</sup> One of this class of materials, CuAlS<sub>2</sub>, is the widest band gap semiconductor [ $E_g=3.49$  eV at 300 K (Ref. 3)] crystallizing in chalcopyrite structure and is an important candidate for blue-to-ultraviolet light emitting device applications.<sup>4</sup>

The Brillouin zone (BZ) center phonon frequencies of CuAlS<sub>2</sub> have been measured by infrared reflectivity<sup>5-7</sup> and Raman scattering<sup>5,6,8-10</sup> spectroscopies at ambient as well as elevated pressures. One interesting point about all these reports is the consistency of data for all the measured mode frequencies, which is not the case for the other Cu-based chalcopyrite semiconductors.<sup>11</sup>

Pressure is used as an important perturbational probe of the electronic, optical, and lattice dynamical properties of materials.<sup>12</sup> Chalcopyrite lattice structure is a deformed super-structure of zinc-blende type structure and the phonon modes at the Brillouin zone center can be mapped to zone center and several zone boundary modes of zinc-blende structure.<sup>13-15</sup> Pressure dependence of lattice dynamical properties of zinc-blende compounds show certain trends, such as a negative mode Grüneisen parameter for transverse acoustic modes, especially towards Brillouin zone boundaries and decrease of effective charges under pressure.<sup>16</sup> In this study, we try to delineate the extent of the relationship between the pressure dependence of lattice dynamical properties of zinc-blende and related ternary compounds. To that end, we investigate the pressure dependence of lattice dynamical properties, such as zone center phonon frequencies, Born effective charges, and dielectric permittivity tensor of chalcopyrite CuAlS<sub>2</sub> using the density functional and density functional perturbation theory.<sup>17-19</sup>

**II. METHOD OF CALCULATION**

The present results have been obtained using the ABINIT code,<sup>20</sup> that is based on pseudopotentials and planewaves. It relies on an efficient fast Fourier transform algorithm<sup>21</sup> for the conversion of wave functions between real and reciprocal

space, on the adaptation to a fixed potential of the band-by-band conjugate gradient method<sup>22</sup> and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential.<sup>23</sup> The exchange-correlation energy is evaluated in local density approximation, using Perdew-Wang parametrization<sup>24</sup> of Ceperley-Adler electron-gas data.<sup>25</sup>

The pseudopotentials have been generated with FHI98PP code.<sup>26</sup> The details of choice of pseudopotentials were reported before for calculations of CuInSe<sub>2</sub>,<sup>27</sup> CuGaS<sub>2</sub>,<sup>28</sup> and CuInS<sub>2</sub>.<sup>29</sup> The kinetic energy cutoff needed to obtain a convergence better than 0.01 eV for total energy is found to be equal to 45 Ha. Changing cutoff from 40 to 45 Ha changes response quantities less than 1%. The Brillouin zone is sampled by 12 special  $k$  points, which is found to be enough for convergence of static as well as response calculations.

Technical details on the computation of responses to atomic displacements and homogeneous electric fields can be found in Ref. 18, while Ref. 19 presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants.

**III. RESULTS****A. Atomic structure**

The details of the geometry of chalcopyrite structure can be found in many papers.<sup>27,30</sup> For self-containment, here we describe the structure of the unit cell briefly. The chalcopyrite structure (space group  $D_{2d}^{12}$ , No. 122) can be considered as derived from the cubic zinc-blende structure (space group  $T_d^2$ ) by populating one of the face centered cubic sublattice with group VI atoms and other one with equal amounts of groups I and III atoms in a regular fashion. In general, I-VI and III-VI bond lengths, denoted by  $d_{I-VI}$  and  $d_{III-VI}$ , respectively, are not equal. One consequence of having two different anion-cation bond lengths is a tetragonal distortion characterized by  $u=0.25+(d_{I-VI}^2-d_{III-VI}^2)/a^2$  which describes the repositioning of the anions in the  $x$ - $y$  plane,  $a$  is the lattice constant in the  $x$  or  $y$  direction. The second consequence of differing anion-cation bond lengths is a deformation of the unit cell to a length  $c$  which is generally different from  $2a$ .

TABLE I. Calculated structural parameters of CuAlS<sub>2</sub> compared to experimental data ( $a$  in a.u.,  $\eta$  and  $u$  are unitless).

	This work	Ref. 9	Ref. 31	Ref. 32	Ref. 33
$a$	9.900	10.082	10.083	10.043	10.076
$\eta$	1.988	1.957	1.958	1.963	1.976
$u$	0.255	0.255	0.268	-	-

This tetragonal distortion is characterized by the quantity  $\eta = c/a$ .

The lattice parameters are determined from atomic and structural relaxation and compared to available experimental values in Table I. Considering the fact that the zero-point motion and thermal effects are not taken into account, the calculated  $a$ ,  $\eta$ , and  $u$  values agree with the experimental values quite well. The bulk modulus and its pressure derivative calculated by fitting to a third-order Vinet equation of state<sup>34</sup> are found to be 974 kbar and 4.5 which are in very good agreement with experimental values of  $990 \pm 30$ ,<sup>8</sup>  $940 \pm 150$ ,<sup>10</sup> and 958.3 kbar.<sup>35</sup>

### B. Born Effective Charge and Dielectric Permittivity Tensors

For insulators, the Born effective charge tensor for atom  $\kappa$ ,  $Z_{\kappa, \beta\alpha}^*$  quantifies, to linear order, the polarization per unit cell, created along the direction  $\beta$  when the atoms of sublattice  $\kappa$  are displaced along the direction  $\alpha$ , under the condition of zero electric field. It can be calculated from Berry phase or perturbation theory.

In Table II, we display dynamical effective charge tensors, eigenvalues of symmetric parts of these tensors, and Grüneisen parameters of these eigenvalues  $\gamma^*$  which is defined as

$$\gamma^* = -\frac{d \ln \lambda}{d \ln V}, \quad (1)$$

where  $V$  is the unit cell volume and  $\lambda$  is the eigenvalue of the symmetric part of relevant effective charge tensor. Because of finite  $k$ -point sampling there is a deviation from charge neutrality which is less than 0.01 electron for the unit cell. The form of effective charge tensor for the constituents is determined by the site symmetry of the ions.  $Z^*$  of cations, which have same site symmetry (they are located at  $4a$  and  $4b$  Wyckoff positions) are almost diagonal with an anisotropy of 4% for Cu and 2% for Al. S ions are located at lower symmetry sites ( $8d$  positions) and as a result their effective charge tensors have nonequivalent diagonal components as well as sizable off-diagonal components. The tetrahedral shifting of anion atoms creates four different configurations for these atoms and the resulting effective charge tensor elements can be divided into two classes according to the direction of the tetrahedral shifting being along  $x$  or  $y$  direction.  $Z_{S,zz}^* = -1.61$  for all anions while  $Z_{S,xx}^*$  and  $Z_{S,yy}^*$  take the value  $-1.53$  or  $-1.67$  depending on the direction of  $u$ . Also, depending on the  $u$  distortion being along  $x$  or  $y$  direction, the off-diagonal components  $Z_{S,zx}^*$ ,  $Z_{S,xz}^*$  or  $Z_{S,yz}^*$ ,  $Z_{S,zy}^*$  are different than zero.

As can be seen from Table II, the Grüneisen parameter for the dynamical effective charges of all the ions are negative, which indicate that  $Z^*$  decreases with increasing pressure. This tendency is an indication of increased metallization under pressure and is found to be the case for almost all zincblende materials, except SiC.<sup>36</sup>

The form of the dielectric tensor is determined by the symmetry of the crystal. Our calculated electronic ( $\epsilon_\infty$ ) and static ( $\epsilon_0$ ) dielectric tensors have two independent components  $\epsilon^\parallel$  and  $\epsilon^\perp$  along and perpendicular to the  $c$  axis, respec-

TABLE II. Calculated Born effective charges of CuAlS<sub>2</sub>. The eigenvalues,  $\lambda$  of the symmetric part of  $Z^*$  are given in brackets. The last column is the Grüneisen parameter,  $\gamma^*$  for the effective charge.

		$\lambda$	$\gamma^*$
$Z_{\text{Cu}}^*$	$\begin{pmatrix} 0.59 & -0.10 & 0.00 \\ 0.10 & 0.59 & 0.00 \\ 0.00 & 0.00 & 0.57 \end{pmatrix}$	$\begin{bmatrix} 0.59 \\ 0.59 \\ 0.57 \end{bmatrix}$	$\begin{bmatrix} -3.73 \\ -3.73 \\ -3.59 \end{bmatrix}$
$Z_{\text{Al}}^*$	$\begin{pmatrix} 2.61 & -0.05 & 0.00 \\ 0.05 & 2.61 & 0.00 \\ 0.00 & 0.00 & 2.66 \end{pmatrix}$	$\begin{bmatrix} 2.66 \\ 2.61 \\ 2.61 \end{bmatrix}$	$\begin{bmatrix} -2.23 \\ -2.23 \\ -0.01 \end{bmatrix}$
$Z_{S_1}^*$	$\begin{pmatrix} -1.53 & 0.00 & 0.00 \\ 0.00 & -1.67 & 0.62 \\ 0.00 & 0.63 & -1.61 \end{pmatrix}$	$\begin{bmatrix} -2.27 \\ -1.53 \\ -1.01 \end{bmatrix}$	$\begin{bmatrix} -0.62 \\ -0.52 \\ -1.31 \end{bmatrix}$
$Z_{S_3}^*$	$\begin{pmatrix} -1.67 & 0.00 & 0.62 \\ 0.00 & -1.53 & 0.00 \\ 0.63 & 0.00 & -1.61 \end{pmatrix}$	$\begin{bmatrix} -2.27 \\ -1.53 \\ -1.01 \end{bmatrix}$	$\begin{bmatrix} -0.62 \\ -0.52 \\ -1.31 \end{bmatrix}$

TABLE III. Static and high frequency dielectric tensor components of CuAlS<sub>2</sub>.

	$\epsilon_{\infty}^{\parallel}$	$\epsilon_{\infty}^{\perp}$	$\epsilon_{\infty}$	$\epsilon_0^{\parallel}$	$\epsilon_0^{\perp}$	$\epsilon_0$
This work	6.81	6.94	6.85	8.84	8.59	8.76
Ref. 5	4.9	5.0	5.0	6.7	6.4	6.5
Ref. 7	4.80	4.90	4.87	7.05	8.14	7.68
Ref. 37	5.1	5.2	5.2	6.9	7.0	7.0

tively. While electronic dielectric tensor is almost isotropic,  $\epsilon_0$  has a small ( $\approx 2.8\%$ ) anisotropy, which is consistent with the fact that for CuAlS<sub>2</sub> tetragonal distortion is very small ( $\eta=c/a \approx 2$ ).

We display our calculated dielectric tensor components along with model calculations of Ref. 37 and experimentally available values in Table III. The averages of  $\epsilon_{\infty}$  and  $\epsilon_0$ , obtained from the expression  $\epsilon_{\infty}$  (or  $\epsilon_0$ ) =  $(2\epsilon_{\infty}^{\perp} + \epsilon_{\infty}^{\parallel})/3$  are also shown in this table.

The infrared data for the electronic part of the dielectric tensor of CuAlS<sub>2</sub> are similar and around 5, but for the static dielectric tensor components there are up to 30% difference between  $\epsilon_0^{\perp}$  reported in Refs. 5 and 7. It is well known that the density functional theory (DFT) overestimates the high-frequency dielectric constants, this is a well-known problem related to underestimation of the band-gap in DFT.<sup>38-40</sup> Our calculated  $\epsilon_{\infty}$  values are somewhat higher than expected overestimation. The agreement for the component of  $\epsilon_0$  is better.

One can define a Grüneisen parameter

$$\gamma^{\epsilon} = -\frac{d \ln \epsilon}{d \ln V} \quad (2)$$

for the pressure dependence of the dielectric constants. We have found  $\gamma^{\epsilon_{\infty}}$ , to be very small negative ( $\gamma^{\epsilon_{\infty}} = -0.0046$ ) for  $\gamma^{\epsilon_{\infty}^{\parallel}}$  and small positive ( $\gamma^{\epsilon_{\infty}^{\perp}} = 0.0081$ ) for  $\epsilon_{\infty}^{\perp}$  components. This is surprising, because  $\gamma^{\epsilon_{\infty}}$  for zinc-blende compounds is much larger than these values.<sup>36</sup> The Grüneisen parameters for the compounds of static dielectric function  $\epsilon_0$  are all negative ( $\gamma^{\epsilon_0^{\perp}} = -0.50$ ,  $\gamma^{\epsilon_0^{\parallel}} = -0.38$ ,  $\gamma^{\epsilon_0} = -0.46$ ) and around those values reported for zinc-blende compounds.<sup>36</sup>

### C. Phonons at $\Gamma$ Point

Since the body-centered tetragonal unit cell of the chalcopyrite structure has eight atoms, there are a total of 24 modes of vibration. A detailed discussion of group theoretical properties of chalcopyrite zone center phonons can be found in Refs. 13 and 28 The irreducible representation at the center of the Brillouin zone is

$$\Gamma_{\text{opt}} = 1\Gamma_1 \oplus 2\Gamma_2 \oplus 3\Gamma_3 \oplus 3\Gamma_4 \oplus 6\Gamma_5$$

for optical modes, and

$$\Gamma_{\text{aco}} = 1\Gamma_4 \oplus 1\Gamma_5$$

for acoustic modes.

In Table IV our calculated zone center phonon frequencies, their symmetry assignments and mode Grüneisen pa-

rameters are displayed and compared with infrared<sup>5-7</sup> and Raman<sup>5,6,8,9</sup> spectroscopic measurements. CuAlS<sub>2</sub> is rather interesting among the Cu-based semiconductors that crystallize in chalcopyrite structure, because, contrary to other members of this family,<sup>11,27,28,41</sup> reports of its zone-center phonon frequencies agree well with each other. As can be seen from the table, based on relative root-mean square (rms) deviation values, our calculated mode frequencies agree very well with the experimental results, especially low temperature Raman measurements reported by Bairamov *et al.*<sup>9</sup> Except for the Andrish *et al.* infrared data,<sup>7</sup> all the rms deviations between our calculated results and the experimental data are within the range of expected accuracy of DFT response calculations.

The Grüneisen parameter  $\gamma_i$  for phonon mode  $i$  is defined as

$$\gamma_i = -\frac{d \ln \omega_i}{d \ln V}, \quad (3)$$

where  $\omega_i$  the frequency of the mode  $i$  and  $V$  is the unit cell volume of the crystal.  $\gamma_i$  expresses the change in phonon frequency under hydrostatic pressure. In Table IV we also display and compare our calculated mode Grüneisen parameters with experimental values reported in Ref. 8. One of the interesting properties of phonons of tetrahedrally coordinated semiconductors of diamond and zinc-blende structure is the pressure softening of their transverse acoustic (TA) modes. Mode Grüneisen parameter for TA modes of Groups IV, III-V, and II-VI compounds that crystallize in diamond and zinc-blende structure are all negative towards the Brillouin zone boundaries.<sup>16</sup> As the chalcopyrite structure is obtained by doubling and deforming the zinc-blende structure, the first Brillouin zone (BZ) of chalcopyrite is formed by folding the zinc-blende BZ. The correspondence between the chalcopyrite zone center phonon modes and modes in zinc-blende structure has been given in Refs. 13-15 and 42 We have found three negative mode Grüneisen parameter for CuAlS<sub>2</sub>, which are two low frequency optical  $\Gamma_5$  and one low frequency  $\Gamma_4$  modes. These modes originate from  $X_{5ac}$ ,  $W_{4ac}$ , and  $W_{2ac}$  modes of zinc-blende structure, respectively.  $\gamma$  for the  $X_{5ac}$ -originated mode is similar in magnitude and sign to values reported for zinc-blende structures.<sup>43-46</sup> Frequency and mode Grüneisen parameters at  $W$  point for zinc-blende materials are, unfortunately, not as well known as those at  $X$  point. From the available data<sup>43</sup> we would expect a smaller, but still negative Grüneisen parameter. Experimental  $\gamma$  for these two modes seem to be very small but positive.

For zinc-blende materials, the mode Grüneisen parameter for longitudinal optical phonons modes ( $\gamma_{TO}$ ) is generally higher than that of transverse optical mode ( $\gamma_{LO}$ ).<sup>43</sup> We have found a similar relationship for CuAlS<sub>2</sub> for the polar mode (the highest frequency  $\Gamma_5$  and  $\Gamma_4$  modes) originating from the zone-center polar mode ( $\Gamma_{15}$ ) of zinc-blende structure.

### IV. CONCLUSION

We have investigated the pressure-dependent lattice dynamical properties, such as Born effective charge tensor,

TABLE IV. Frequencies of phonons and mode Grüneisen parameters at the  $\Gamma$  point ( $\omega$  in  $\text{cm}^{-1}$ ). All experimental data, except those indicated in the footnote, are room temperature measurements.

Mode	<i>Ab initio</i>		Experiment								$\gamma_i$		
	Present	IR <sup>5</sup>	IR <sup>6</sup>	IR <sup>7</sup>	R <sup>5</sup>	R <sup>8</sup>	R <sup>a</sup>	R <sup>9</sup>	R <sup>b</sup>	R <sup>10</sup>	Present	Ref. 8	Ref. 10
$\Gamma_1$	325				315	315	316	314	317	315	1.5	1.5	1.6±0.2
$\Gamma_2$	366										1.4		
$\Gamma_2$	304										1.4		
$\Gamma_3$	448					440	443	442	448		1.6	1.4	
$\Gamma_3$	263				268	268	269	263	266		0.9	0.7	
$\Gamma_3$	115				98	98	102	96			0.8	0.9	
$\Gamma_{4TO}^{LO}$	495	498		500	497	495		498	503		1.4	1.1	
	453	446	446	456	445	456	446	446	448		1.7	1.3	
$\Gamma_{4TO}^{LO}$	296	284		285	278	270					1.9	2.7	
	287	271	271	264	266	270	267	272	274		1.7	2.7	
$\Gamma_{4TO}^{LO}$	120			111	112	111		108			-0.1	0.1	
	119		114	105	112	111	114	108			-0.3	0.1	
$\Gamma_{5TO}^{LO}$	489	497	497	496	494	495	499	496	498		1.3	1.1	
	449	444	444	452	445	444	444	444	449		1.7	1.5	
$\Gamma_{5TO}^{LO}$	440	432		434		420					1.7	1.5	
	436	432	432	430		373	433				1.5	1.0	
$\Gamma_{5TO}^{LO}$	290	266	266	242	265	266	267	263	275		1.8	2.2	
	287	263	263	228	262	266	265	261	265	265	1.9	2.2	1.9±0.3
$\Gamma_{5TO}^{LO}$	218	217	217	220	219	220	220	218	220		1.2	0.6	
	218	216	216	208	218	220	218	218	220	218	1.2	0.6	0.8±0.2
$\Gamma_{5TO}^{LO}$	146		140			150	142	135			-0.1	0.2	
	146		140			150	142	135			-0.1	0.2	
$\Gamma_{5TO}^{LO}$	83		77		76	78	78	76	77		-1.1	-0.6	
	83		77		76	78	78	74	77	76	-1.2	-0.6	≤±0.3
rms relative deviations													
		0.046	0.056	0.103	0.073	0.072	0.056	0.083	0.045	0.062			

<sup>a</sup>Reference 6 (at 78 K).<sup>b</sup>Reference 9 (at 8 K).

Brillouin zone center phonon frequencies, and static and high frequency dielectric tensors of ternary semiconductor  $\text{CuAlS}_2$  within the density functional perturbation theory framework. We have found that the pressure dependence of these quantities show similar trends with binary tetrahedrally coordinated compounds. Under hydrostatic pressure, the dy-

namical effective charges decrease. The zone center modes originating from the modes with negative Grüneisen parameter in zinc-blende materials, have negative Grüneisen parameters and the ordering of  $\gamma_{TO} > \gamma_{LO}$  is respected for the zone-center chalcopyrite modes that originate from the zone-center polar mode of zinc-blende structure.

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